

# PATENT ABSTRACTS OF JAPAN

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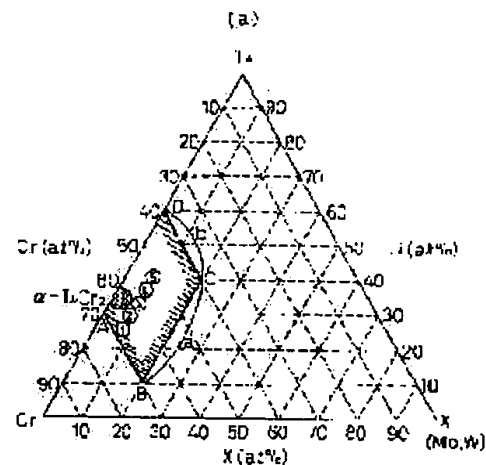
IBA HIDENORI

## (54) HYDROGEN STORAGE ALLOY AND ITS PRODUCTION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a hydrogen storage alloy requiring no particular use of expensive alloying elements such as V, having a hydrogen absorbing and releasing capacity equal to that of the conventional BCC type hydrogen storage alloy, and advantageous in respect of manufacturing costs, and its production.

**SOLUTION:** The hydrogen storage alloy has a composition represented by formula  $Ti_{100-a-b}Cr_aX_b$  [where X is at least either of Mo and W and the symbols (a) and (b) satisfy, by atomic %,  $40 \leq a \leq 70$  and  $0 < b \leq 20$ , respectively] and also has a crystalline cubic structure composed of body-centered structure (BCC type). As the method of manufacture of this hydrogen storage alloy, the aforesaid alloy is melted and cast, and the resultant ingot is held at  $1200-1400^\circ\text{C}$  (excluding TiCr single phase region) for 1-5hr and then subjected to rapid cooling treatment, by which the crystalline structure is provided with body-centered cubic structure (BCC type) at ordinary temp.



(b)

	Ti (at.%)	Cr (at.%)	X (at.%)
①	77	95	?
②	30	63	?
③	33	60	?
④	36	57	?
⑤	39	54	?

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**CLAIMS**

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[Claim(s)]

[Claim 1] Composition is the hydrogen storing metal alloy which general formula  $Ti_{100-a-b}Cr_aX_b$ , however X are at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and is expressed with  $40 \leq a \leq 70$  and  $0 < b \leq 20$ , and is characterized by the crystal structure being a body centered cubic structure (BCC type).

[Claim 2] The manufacture method of the hydrogen storing metal alloy characterized by making as [ have / a body centered cubic structure (BCC type) / the crystal structure / by holding the alloy of a claim 1 after the dissolution / casting, holding this ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, a TiCr<sub>2</sub> single-phase field is removed), and performing quenching processing after that / in ordinary temperature ].

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Without using alloy elements, such as expensive V, especially about a hydrogen storing metal alloy, this invention has hydrogen \*\*\*\*\* of the conventional BCC type hydrogen storing metal alloy and this level, and relates to the advantageous hydrogen storing metal alloy in manufacturing cost, and its manufacture method.

[0002]

[Description of the Prior Art] or [that occlusion of the hydrogen gas of about 1000 times or more of own volume of an alloy is carried out, a hydrogen storing metal alloy can store it as a storage / transportation means of hydrogen, and the volume density is almost equivalent to a liquid or solid-state hydrogen] -- or it is more than it LaNi<sub>5</sub> by which the metal of body centered cubic structures (Following BCC is called), such as V, Nb, Ta, and a TiVMn system, a TiVCr system alloy, is already put in practical use as this hydrogen-absorption material etc. -- AB<sub>5</sub> type alloy and TiMn<sub>2</sub> etc. -- AB<sub>2</sub> Compared with the type alloy, carrying out occlusion of a lot of hydrogen was known for many years. This is because there are many hydrogen-absorption sites in the crystal lattice and the hydrogen storage capacity by calculation is very as large as H/M=2.0 (alloys, such as Ti, V, etc. which are about 50 atomic weight, about 4.0 wt(s)%) with BCC structure.

[0003] Moreover, in a pure vanadium alloy, occlusion of the almost same about 4.0 wt(s)% as the value calculated from the crystal structure is carried out, and the abbreviation half is emitted under an ordinary temperature ordinary pressure. It is known that big hydrogen storage capacity and a good hydrogen-desorption property are similarly shown in 5A group's Nb and Ta of an element of the same periodic table. However, at pure metals, such as V, Nb, and Ta, since cost is very high, the property has been examined in the alloy of the component range which has BCC structures, such as Ti-V, by the industrial application which needs a certain amount of amounts of alloys, such as a hydrogen tank and an nickel-MH cell. The hydrogen storing metal alloy which has the capacity of equivalent level, without including V to this since all contain expensive V, although the BCC type hydrogen storing metal alloy which contains such Ti on the other hand is high capacity can expect an epoch-making cost merit in the application which needs a high capacity hydrogen tank [for electric vehicle (EV)] hydrogen storing metal alloy.

[0004] Moreover, although V is eluted in the electrolytic solution in an nickel-MH cell, with the alloy which does not contain this, application to the negative-electrode material of an nickel-MH cell is also expectable. as well-known technology of this field, to JP,4-210446,A, hydrogen storage capacity is increased with the comparatively cheap cost of materials, and it is indicated in the TiCrMo system and the TiCrMoFe system for the purpose of enlarging a reaction rate further that -40-degree C hydrogen \*\*\*\*\*, the efficiency which is occlusion and discharge further, and a reaction rate are arc-dissolution-improvable under high grade Ar gas atmosphere Moreover, to JP,61-176067,A, a kind of element chosen as a Ti-Cr alloy from alkaline earth metal etc. is added, and the hydrogen storing metal alloy for offering the long metal hydride electrode of the cycle life by charge and discharge is indicated.

[0005] However, in addition to the point of difficulty in activation that the reaction rate made into the problem in V system is slow, with these BCC alloys, new troubles, like there are few burst sizes only by carrying out occlusion by practical temperature and pressure are also produced. Consequently, the alloy which makes a BCC phase a main composition phase has not yet resulted in practical use. Furthermore, development of the alloy in which did not contain expensive alloy elements, such as V, and hydrogen \*\*\*\*\* was excellent is desired.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention examines replacing V in the Ti-V-Mn system of the conventional BCC type hydrogen storing metal alloy, and a Ti-V-Cr system alloy by Mo and/or W,

and offers a cheap hydrogen storing metal alloy by high capacity. Moreover, other purposes of this invention are [aforementioned] advantageous in manufacturing cost, and offer the hydrogen storing metal alloy which has hydrogen \*\*\*\*\* whose application in a industrial scale is enabled as a hydrogen tank or an object for nickel-MH cells with the alloy excellent in hydrogen \*\*\*\*\* . Moreover, another purpose of this invention attains the optimal manufacturing process for enabling manufacture in a industrial scale by the low cost with the above-mentioned new BCC alloy by the heat treatment method.

[0007]

[Means for Solving the Problem] As for the above-mentioned purpose, composition of general formula  $Ti_{100-a-b}Cr_aX_b$ , however X is at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and it is attained by the hydrogen storing metal alloy which is expressed with  $40 \leq a \leq 70$  and  $0 < b \leq 20$ , and is characterized by the crystal structure being a body centered cubic structure (BCC type). Moreover, it is attained also by the manufacture method of the hydrogen storing metal alloy characterized by making as [have / a body centered cubic structure (BCC type) / the crystal structure / in ordinary temperature] by the above-mentioned purpose's holding the aforementioned alloy after the dissolution / casting, holding the aforementioned ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, a TiCr<sub>2</sub> single-phase field is removed), and carrying out quenching processing after that.

[0008]

[Embodiments of the Invention] As an example of the alloy of this invention, the range of an Ti-Cr-Mo system alloy is shown in drawing 1. this 3 yuan state diagram -- TiCr<sub>2</sub> of a Ti-Cr system it is -- the single phase field of a Laves phase exists and let this invention be the range which this range is avoided and the crystal structure becomes from BCC namely, within the limits surrounded by the points A (Ti<sub>30</sub>Cr<sub>70</sub>) and B (Ti<sub>10</sub>Cr<sub>70</sub>X<sub>20</sub>) of drawing 1, and the segment which consists of C (Ti<sub>40</sub>Cr<sub>40</sub>X<sub>20</sub>) and D (Ti<sub>60</sub>Cr<sub>40</sub>) -- however, segments other than AD -- it considers as composition including a top

[0009] On the other hand, with the alloy regularly disassembled into the detailed two phase of nano order by the spinodal decomposition in the interior also in the BCC alloy in an old this invention person's etc. knowledge, a hydrogen-desorption property is improved remarkably. the duality used as the foundations of this ternary alloy -- it is a system state diagram and it turns out especially by the Ti-Cr system, the Cr-Mo system, and the Cr-W system that the field of two-phase separation exists The state diagram of the duality of a Ti-Cr system is shown in drawing 6 as an example. In this drawing, it is TiCr<sub>2</sub>. There is the solidus line of the two-phase separation which connects 1370 degrees C and an eutectoid point, and it is a uniform BCC phase at the temperature beyond this. In such a state diagram, the two phase from which the lattice constant which was formed of the spinodal decomposition and grew up to be specific crystal orientation differs will have periodic structure at intervals of 1.0 to 100nm.

[0010] According to this regular nano order period structure, the big hydrogen storage capacity which a BCC alloy has structurally can be made to be able to emit in practical temperature and a pressure region, and activation conditions can be eased, and a reaction rate can be improved. It is TiCr<sub>2</sub> of drawing 5 that the existence region of the BCC uniform phase in the alloy system of this invention was shown more concretely on the other hand. It is the pseudo-binary diagram which set Mo as the third element, and/or W to X. The heat treatment temperature of this invention is the portion TiCr<sub>2</sub> displayed with a slash, i.e., the above, in this drawing. A single phase field is excepted and it considers as the range which can be come uniformly with BCC to a room temperature.

[0011] As mentioned above, this invention enables offer of the conventional BCC type hydrogen storing metal alloy and the alloy which has hydrogen \*\*\*\*\* of this level, without using expensive V. Furthermore, low-cost-ization by optimization of a manufacturing process is also enabled. Next, alloy composition and the heat treatment conditions of this invention are explained. Since alloy composition of this invention uses Ti, Cr, Mo, and/or W as a component, as compared with the hydrogen storing metal alloy which used the conventional V etc., it is the component which reduced cost and replaced V etc. by Mo and/or W, and the solution treatment range in a state diagram is expanded, therefore phase separation fully happens, and the alloy which was excellent in the two phase state at hydrogen \*\*\*\*\* is obtained. Hereafter, the reason for component limitation of this invention is explained. General formula  $Ti_{100-a-b}Cr_aX_b$ , however X are atomic % displays, and are expressed with  $40 \leq a \leq 70$  and  $0 < b \leq 20$  by the inside a and b of Mo and/or W, and a formula. The aforementioned composition range optimizes equalization of a BCC phase, and distortion of the crystal structure in the two-phase separation state in the alloy by heat treatment, and can call them the optimal composition which the detailed organization which enables promotion of the mobility of the hydrogen as a hydrogen storing metal alloy can do.

[0012] That is, the equilibrium pressure force [in / the hydrogen \*\*\*\*\* (pressure composition constant-temperature-line-CT diagram) of a hydrogen storing metal alloy / less than / 40at% / in Cr] is low, and it becomes difficult to take out again the hydrogen which carried out occlusion in ordinary temperature. Moreover, the

aforementioned equilibrium pressure force has [ Cr ] little hydrogen storage capacity in high 11 ordinary temperature at 70at% \*\*. Furthermore, an alloy is not BCC-ized even if Mo and/or W heat-treat at 0at%. Since hydrogen storage capacity falls, it becomes moreover, less practical in 20at% \*\*. For this reason, it limited to the above-mentioned composition range. Mo and/or the desirable range of W are 20% or less 5% or more. Moreover, the desirable range of Cr is 70% or less 50% or more.

[0013] By this invention, the BCC phase appeared the aforementioned alloy uniformly, and the heat treatment conditions as the manufacture method were specified so that hydrogen \*\*\*\*\* might be made into the maximum. That is, it is characterized by BCC-izing an alloy by holding a hardener after the dissolution / casting, holding the aforementioned ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, a TiCr<sub>2</sub> single-phase field is removed), and carrying out quenching processing in an oil or iced water after that. That is, as heat treatment conditions for this invention, a high capacity hydrogen storage capacity BCC phase will exist in stability only in 1200 degrees C or more in the alloy of the above-mentioned composition range. On the other hand, the alloy in which melting was carried out by the IH method, the arc solution process, etc. usually metamorphoses into more stable C14 Laves phase below 1200 degrees C at the time of cooling. for this reason -- in order to form a BCC phase by the above-mentioned composition -- an elevated temperature -- it is necessary to freeze a stable BCC phase to ordinary temperature

[0014]

[Example] The sample of a hydrogen storing metal alloy was created as follows as an example of this invention. Composition is \*\*Ti<sub>27</sub>Cr<sub>66</sub>Mo<sub>7</sub> shown in drawing 1 (b), \*\*Ti<sub>30</sub>Cr<sub>63</sub>Mo<sub>7</sub>, \*\*Ti<sub>33</sub>Cr<sub>60</sub>Mo<sub>7</sub>, \*\*Ti<sub>36</sub>Cr<sub>57</sub>Mo<sub>7</sub>, and \*\*Ti<sub>39</sub>Cr<sub>54</sub>Mo<sub>7</sub> as the range of this invention, i.e., a composition range in ABCD of drawing 1 (a). The quality governing was carried out. About 20g ingot performed all samples by the arc dissolution in an argon which used water-cooled copper Haas. After heating at 1400 degrees C after casting for 2 hours, heat treatment which carries out water cooling is performed, an organization is set to BCC, this ingot is ground in air, and all the data of this example are 60 degrees C and 10-4torr vacuum length +50atm as activation. After carrying out the four-cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and hydrogen \*\*\*\*\* of an alloy are performed by the PCT measurement based on the vacuum condition specified for the pressure composition constant-temperature-line measuring method (JIS H7201) by the constant volume method.

[0015] Moreover, structural analysis of an alloy was performed using EDX (energy-dispersion type X diffraction) of a transmission electron microscope and attachment. The crystal structure model was created based on the information furthermore acquired with the transmission electron microscope, and lied belt analysis of powder X diffraction data was performed. Lied belt analysis can be asked for the weight fraction of each phase by calculation while it can carry out elaboration of the crystal structure parameter using diffraction intensity unlike the usual X-ray diffraction method. Analysis soft RIETAN94 which the National Institute for Research in Inorganic Materials spring doctor developed was used for lied belt analysis.

[0016] Drawing 2 is drawing showing 0-degree C the hydrogen absorption and discharge process about the sample of the aforementioned [ of this example ] \*\* - \*\*. In this drawing, it is \*\*Ti<sub>27</sub>Cr<sub>66</sub>Mo<sub>7</sub>. And \*\*Ti<sub>30</sub>Cr<sub>63</sub>Mo<sub>7</sub> Hydrogen storage capacity hardly emits small. \*\* Ti<sub>33</sub>Cr<sub>60</sub>Mo<sub>7</sub> And \*\*Ti<sub>36</sub>Cr<sub>57</sub>Mo<sub>7</sub> Hydrogen storage capacity is then improved and it is \*\*Ti<sub>33</sub>Cr<sub>60</sub>Mo<sub>7</sub>. The Prato equilibrium pressure is about 1 MPa. Near and \*\*Ti<sub>36</sub>Cr<sub>57</sub>Mo<sub>7</sub> It is 1MPa then. It is the following, and occlusion and discharge show the greatest value and shows the good value also in Prato flat nature. Moreover, \*\*Ti<sub>39</sub>Cr<sub>54</sub>Mo<sub>7</sub> If it attaches, hydrogen storage capacity is small and the hardly emitted inclination is shown. drawing 3 -- aforementioned \*\*Ti<sub>39</sub>Cr<sub>54</sub>Mo<sub>7</sub> \*\*\*\*\* -- the hydrogen-absorption property in 0 degree C and 40 degrees C is shown In this component, hydrogen storage capacity and the burst size have been improved in 40 degrees C, and the flat nature in the Prato \*\* is also a quite good result, and this component system found that it was promising practically.

[0017] The pressure (Prato equilibrium pressure) of the flat field of the pressure composition constant-temperature line changes with the composition ratios of Ti/Cr, as shown in drawing 8 (a) and (b). This drawing fixes Mo of an Ti-Cr-Mo system to 7at(s)%, and changes the amount of Ti and Cr. They are 0.01MPa(s) at the alloy composition which shows the absorption pressure of 10 or less MPas by this invention at -40 degrees C considered as an operating environment of applications, such as a hydrogen tank and heat pump, and 100 degrees C. Alloy composition which shows the above desorption pressure was made into the generic claim.

[0018] Moreover, the hydrogen absorption and discharge process (PCT property) of a sample which heat treatment of water quenching was performed to drawing 4 after 2-hour maintenance at 1400 degrees C after the arc dissolution like the above about Ti<sub>41</sub>Cr<sub>56</sub> W<sub>3</sub> are shown. This drawing shows 40-degree C maximum hydrogen storage capacity about 2.3 Wt(s)%, it shows an about 2.4 Wt(s)% good value at 0 degree C, and 40 degrees C shows the result also with the quite good flat nature in the Prato \*\* also in the emission characteristic. drawing 3

and drawing 4 -- abbreviation -- it is the same hydrogen-absorption property, and from this, by W, since it is twice [ about ] the atomic weight of this as compared with Mo, an addition is considered that a BCC-ized effect is because it is fully obtained at least Comparison of hydrogen \*\*\*\*\* of this invention material and comparison material is shown in Table 1.

[0019]

[Table 1]

試 料	組 成	水素吸蔵量(cc/g)	水素放出量(cc/g)
発明材	Ti <sub>33</sub> Cr <sub>60</sub> Mo <sub>7</sub>	598	423
	Ti <sub>36</sub> Cr <sub>57</sub> Mo <sub>7</sub>	674	502
比較材	Ti <sub>20</sub> Cr <sub>73</sub> Mo <sub>7</sub>	146	40

[0020] From this table, it is Ti33Cr60Mo7 of this invention. A burst size is 598 cc/g in 598 cc/g then, and hydrogen storage capacity is Ti36Cr57Mo7. Hydrogen storage capacity is 674 cc/g then, and the burst size shows 502 cc/g and the good value. On the other hand, at Ti20Cr73Mo7 of comparison material, as for the burst size, hydrogen storage capacity shows the quite small value by 146 cc/g as compared with 40 cc/g and the aforementioned this invention material. Clearly, this invention material has more available-hydrogen movement magnitude than a RABESU alloy, is excellent in hydrogen \*\*\*\*\* , and is the BCC alloy and this level containing V of the former [ weighted solidity / the ]. moreover, the table 2 -- composition \*\*Ti36Cr57Mo7 \*\*\*\*\* -- comparison shows the phase molar fraction of the BCC and the Laves phase by XRD after a hardener and heat treatment [0021] The chart of the X-ray relative intensity of XRD (Cu electrode, output 48kv) about Ti41Cr56 W3 and the degree of angle of diffraction is shown in drawing 7 (a) and (b). (a) Drawing is a sample immediately after the arc dissolution, and the (b) view is a result about heat treatment material (1400 degrees C -> water cooling). Although the phase existed in addition to this with the Laves phase immediately after the arc dissolution, it turns out that it is BCC uniform single phase with heat treatment.

[0022]

[Table 2]

	B C C	ラーベス
母合金	0	100
1300℃×2hr-油冷	86	14

[0023] The alloy heat-treated from this to a hardener being RABESU single phase is understood that it has BCC-ized notably.

[0024]

[Effect of the Invention] By this invention, manufacture of the BCC type hydrogen storing metal alloy which is the same level as [ in which hydrogen \*\*\*\*\* contains the conventional V etc. ] an alloy is attained, without including expensive V etc. Moreover, drastic curtailment of alloy raw material expense can be aimed at. Therefore, by this invention, a high capacity BCC type hydrogen storing metal alloy can be extremely manufactured by the low cost, and the utilization to various uses is attained.

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TECHNICAL FIELD

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[The technical field to which invention belongs] Without using alloy elements, such as expensive V, especially about a hydrogen storing metal alloy, this invention has hydrogen \*\*\*\*\* of the conventional BCC type hydrogen storing metal alloy and this level, and relates to the advantageous hydrogen storing metal alloy in manufacturing cost, and its manufacture method.

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PRIOR ART

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[Description of the Prior Art] or [that occlusion of the hydrogen gas of about 1000 times or more of own volume of an alloy is carried out, a hydrogen storing metal alloy can store it as a storage / transportation means of hydrogen, and the volume density is almost equivalent to a liquid or solid-state hydrogen] -- or it is more than it LaNi<sub>5</sub> by which the metal of body centered cubic structures (Following BCC is called), such as V, Nb, Ta, and a TiVMn system, a TiVCr system alloy, is already put in practical use as this hydrogen-absorption material etc. -- AB<sub>5</sub> type alloy and TiMn<sub>2</sub> etc. -- AB<sub>2</sub> Compared with the type alloy, carrying out occlusion of a lot of hydrogen was known for many years. This is because there are many hydrogen-absorption sites in the crystal lattice and the hydrogen storage capacity by calculation is very as large as H/M=2.0 (alloys, such as Ti, V, etc. which are about 50 atomic weight, about 4.0 wt(s)%) with BCC structure.

[0003] Moreover, in a pure vanadium alloy, occlusion of the almost same about 4.0 wt(s)% as the value calculated from the crystal structure is carried out, and the abbreviation half is emitted under an ordinary temperature ordinary pressure. It is known that big hydrogen storage capacity and a good hydrogen-desorption property are similarly shown in 5A group's Nb and Ta of an element of the same periodic table. However, at pure metals, such as V, Nb, and Ta, since cost is very high, the property has been examined in the alloy of the component range which has BCC structures, such as Ti-V, by the industrial application which needs a certain amount of amounts of alloys, such as a hydrogen tank and an nickel-MH cell. The hydrogen storing metal alloy which has the capacity of equivalent level, without including V to this since all contain expensive V, although the BCC type hydrogen storing metal alloy which contains such Ti on the other hand is high capacity can expect an epoch-making cost merit in the application which needs a high capacity hydrogen tank [ for electric vehicle (EV) ] hydrogen storing metal alloy.

[0004] Moreover, although V is eluted in the electrolytic solution in an nickel-MH cell, with the alloy which does not contain this, application to the negative-electrode material of an nickel-MH cell is also expectable. as well-known technology of this field, to JP,4-210446,A, hydrogen storage capacity is increased with the comparatively cheap cost of materials, and it is indicated in the TiCrMo system and the TiCrMoFe system for the purpose of enlarging a reaction rate further that -40-degree C hydrogen \*\*\*\*\*, the efficiency which is occlusion and discharge further, and a reaction rate are arc-dissolution-improvable under high grade Ar gas atmosphere Moreover, to JP,61-176067,A, a kind of element chosen as a Ti-Cr alloy from alkaline earth metal etc. is added, and the hydrogen storing metal alloy for offering the long metal hydride electrode of the cycle life by charge and discharge is indicated.

[0005] However, in addition to the point of difficulty in activation that the reaction rate made into the problem in V system is slow, with these BCC alloys, new troubles, like there are few burst sizes only by carrying out occlusion by practical temperature and pressure are also produced. Consequently, the alloy which makes a BCC phase a main composition phase has not yet resulted in practical use. Furthermore, development of the alloy in which did not contain expensive alloy elements, such as V, and hydrogen \*\*\*\*\* was excellent is desired.

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EFFECT OF THE INVENTION

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[Effect of the Invention] By this invention, manufacture of the BCC type hydrogen storing metal alloy which is the same level as [ in which hydrogen \*\*\*\*\* contains the conventional V etc. ] an alloy is attained, without including expensive V etc. Moreover, drastic curtailment of alloy raw material expense can be aimed at. Therefore, by this invention, a high capacity BCC type hydrogen storing metal alloy can be extremely manufactured by the low cost, and the utilization to various uses is attained.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The purpose of this invention examines replacing V in the Ti-V-Mn system of the conventional BCC type hydrogen storing metal alloy, and a Ti-V-Cr system alloy by Mo and/or W, and offers a cheap hydrogen storing metal alloy by high capacity. Moreover, other purposes of this invention are [aforementioned] advantageous in manufacturing cost, and offer the hydrogen storing metal alloy which has hydrogen \*\*\*\*\* whose application in a industrial scale is enabled as a hydrogen tank or an object for nickel-MH cells with the alloy excellent in hydrogen \*\*\*\*\* . Moreover, another purpose of this invention attains the optimal manufacturing process for enabling manufacture in a industrial scale by the low cost with the above-mentioned new BCC alloy by the heat treatment method.

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MEANS

[Means for Solving the Problem] As for the above-mentioned purpose, composition of general formula  $Ti_{100-a-b}Cr_aX_b$ , however X is at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and it is attained by the hydrogen storing metal alloy which is expressed with  $40 \leq a \leq 70$  and  $0 < b \leq 20$ , and is characterized by the crystal structure being a body centered cubic structure (BCC type). Moreover, it is attained also by the manufacture method of the hydrogen storing metal alloy characterized by making as [ have / a body centered cubic structure (BCC type) / the crystal structure / in ordinary temperature ] by the above-mentioned purpose's holding the aforementioned alloy after the dissolution / casting, holding the aforementioned ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, a TiCr<sub>2</sub> single-phase field is removed), and carrying out quenching processing after that.

[0008]

[Embodiments of the Invention] As an example of the alloy of this invention, the range of an Ti-Cr-Mo system alloy is shown in drawing 1. this 3 yuan state diagram -- TiCr<sub>2</sub> of a Ti-Cr system it is -- the single phase field of a Laves phase exists and let this invention be the range which this range is avoided and the crystal structure becomes from BCC namely, within the limits surrounded by the points A (Ti<sub>30</sub>Cr<sub>70</sub>) and B (Ti<sub>10</sub>Cr<sub>70</sub>X<sub>20</sub>) of drawing 1, and the segment which consists of C (Ti<sub>40</sub>Cr<sub>40</sub>X<sub>20</sub>) and D (Ti<sub>60</sub>Cr<sub>40</sub>) -- however, segments other than AD -- it considers as composition including a top

[0009] On the other hand, with the alloy regularly disassembled into the detailed two phase of nano order by the spinodal decomposition in the interior also in the BCC alloy in an old this invention person's etc. knowledge, a hydrogen-desorption property is improved remarkably. the duality used as the foundations of this ternary alloy -- it is a system state diagram and it turns out especially by the Ti-Cr system, the Cr-Mo system, and the Cr-W system that the field of two-phase separation exists The state diagram of the duality of a Ti-Cr system is shown in drawing 6 as an example. In this drawing, it is TiCr<sub>2</sub>. There is the solidus line of the two-phase separation which connects 1370 degrees C and an eutectoid point, and it is a uniform BCC phase at the temperature beyond this. In such a state diagram, the two phase from which the lattice constant which was formed of the spinodal decomposition and grew up to be specific crystal orientation differs will have periodic structure at intervals of 1.0 to 100nm.

[0010] According to this regular nano order period structure, the big hydrogen storage capacity which a BCC alloy has structurally can be made to be able to emit in practical temperature and a pressure region, and activation conditions can be eased, and a reaction rate can be improved. It is TiCr<sub>2</sub> of drawing 5 that the existence region of the BCC uniform phase in the alloy system of this invention was shown more concretely on the other hand. It is the pseudo-binary diagram which set Mo as the third element, and/or W to X. The heat treatment temperature of this invention is the portion TiCr<sub>2</sub> displayed with a slash, i.e., the above, in this drawing. A single phase field is excepted and it considers as the range which can be come uniformly with BCC to a room temperature.

[0011] As mentioned above, this invention enables offer of the conventional BCC type hydrogen storing metal alloy and the alloy which has hydrogen \*\*\*\*\* of this level, without using expensive V. Furthermore, low-cost-ization by optimization of a manufacturing process is also enabled. Next, alloy composition and the heat treatment conditions of this invention are explained. Since alloy composition of this invention uses Ti, Cr, Mo, and/or W as a component, as compared with the hydrogen storing metal alloy which used the conventional V etc., it is the component which reduced cost and replaced V etc. by Mo and/or W, and the solution treatment range in a state diagram is expanded, therefore phase separation fully happens, and the alloy which was excellent in the two phase state at hydrogen \*\*\*\*\* is obtained. Hereafter, the reason for component limitation of this invention is explained. General formula  $Ti_{100-a-b}Cr_aX_b$ , however X are atomic % displays, and are expressed with  $40 \leq a \leq 70$  and  $0 < b \leq 20$  by the inside a and b of Mo and/or W, and a formula. The aforementioned composition range optimizes equalization of a BCC phase, and distortion of the crystal structure in the two-phase separation

state in the alloy by heat treatment, and can call them the optimal composition which the detailed organization which enables promotion of the mobility of the hydrogen as a hydrogen storing metal alloy can do.

[0012] That is, the equilibrium pressure force [ in / the hydrogen \*\*\*\*\* (pressure composition constant-temperature-line-CT diagram) of a hydrogen storing metal alloy / less than / 40at% / in Cr ] is low, and it becomes difficult to take out again the hydrogen which carried out occlusion in ordinary temperature. Moreover, the aforementioned equilibrium pressure force has [ Cr ] little hydrogen storage capacity in high 11 ordinary temperature at 70at% \*\*. Furthermore, an alloy is not BCC-ized even if Mo and/or W heat-treat at 0at%. Since hydrogen storage capacity falls, it becomes moreover, less practical in 20at% \*\*. For this reason, it limited to the above-mentioned composition range. Mo and/or the desirable range of W are 20% or less 5% or more. Moreover, the desirable range of Cr is 70% or less 50% or more.

[0013] By this invention, the BCC phase appeared the aforementioned alloy uniformly, and the heat treatment conditions as the manufacture method were specified so that hydrogen \*\*\*\*\* might be made into the maximum. That is, it is characterized by BCC-izing an alloy by holding a hardener after the dissolution / casting, holding the aforementioned ingot for 1 to 5 hours at the temperature of 1200-1400 degrees C (however, a TiCr<sub>2</sub> single-phase field is removed), and carrying out quenching processing in an oil or iced water after that. That is, as heat treatment conditions for this invention, a high capacity hydrogen storage capacity BCC phase will exist in stability only in 1200 degrees C or more in the alloy of the above-mentioned composition range. On the other hand, the alloy in which melting was carried out by the IH method, the arc solution process, etc. usually metamorphoses into more stable C14 Laves phase below 1200 degrees C at the time of cooling. for this reason -- in order to form a BCC phase by the above-mentioned composition -- an elevated temperature -- it is necessary to freeze a stable BCC phase to ordinary temperature

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[Translation done.]

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EXAMPLE

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[Example] The sample of a hydrogen storing metal alloy was created as follows as an example of this invention. Composition is \*\*Ti<sub>27</sub>Cr<sub>66</sub>Mo<sub>7</sub> shown in drawing 1 (b), \*\*Ti<sub>30</sub>Cr<sub>63</sub>Mo<sub>7</sub>, \*\*Ti<sub>33</sub>Cr<sub>60</sub>Mo<sub>7</sub>, \*\*Ti<sub>36</sub>Cr<sub>57</sub>Mo<sub>7</sub>, and \*\*Ti<sub>39</sub>Cr<sub>54</sub>Mo<sub>7</sub> as the range of this invention, i.e., a composition range in ABCD of drawing 1 (a). The quality governing was carried out. About 20g ingot performed all samples by the arc dissolution in an argon which used water-cooled copper Haas. After heating at 1400 degrees C after casting for 2 hours, heat treatment which carries out water cooling is performed, an organization is set to BCC, this ingot is ground in air, and all the data of this example are 60 degrees C and 10-4torr vacuum length +50atm as activation. After carrying out the four-cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and hydrogen \*\*\*\*\* of an alloy are performed by the PCT measurement based on the vacuum condition specified for the pressure composition constant-temperature-line measuring method (JIS H7201) by the constant volume method.

[0015] Moreover, structural analysis of an alloy was performed using EDX (energy-dispersion type X diffraction) of a transmission electron microscope and attachment. The crystal structure model was created based on the information furthermore acquired with the transmission electron microscope, and lied belt analysis of powder X diffraction data was performed. Lied belt analysis can be asked for the weight fraction of each phase by calculation while it can carry out elaboration of the crystal structure parameter using diffraction intensity unlike the usual X-ray diffraction method. Analysis soft RIETAN94 which the National Institute for Research in Inorganic Materials spring doctor developed was used for lied belt analysis.

[0016] Drawing 2 is drawing showing 0-degree C the hydrogen absorption and discharge process about the sample of the aforementioned [ of this example ] \*\* - \*\*. In this drawing, it is \*\*Ti<sub>27</sub>Cr<sub>66</sub>Mo<sub>7</sub>. And \*\*Ti<sub>30</sub>Cr<sub>63</sub>Mo<sub>7</sub> Hydrogen storage capacity hardly emits small. \*\* Ti<sub>33</sub>Cr<sub>60</sub>Mo<sub>7</sub> And \*\*Ti<sub>36</sub>Cr<sub>57</sub>Mo<sub>7</sub> Hydrogen storage capacity is then improved and it is \*\*Ti<sub>33</sub>Cr<sub>60</sub>Mo<sub>7</sub>. The Prato equilibrium pressure is about 1 MPa. Near and \*\*Ti<sub>36</sub>Cr<sub>57</sub>Mo<sub>7</sub> It is 1MPa then. It is the following, and occlusion and discharge show the greatest value and shows the good value also in Prato flat nature. Moreover, \*\*Ti<sub>39</sub>Cr<sub>54</sub>Mo<sub>7</sub> If it attaches, hydrogen storage capacity is small and the hardly emitted inclination is shown. drawing 3 -- aforementioned \*\*Ti<sub>39</sub>Cr<sub>54</sub>Mo<sub>7</sub> \*\*\*\*\* -- the hydrogen-absorption property in 0 degree C and 40 degrees C is shown In this component, hydrogen storage capacity and the burst size have been improved in 40 degrees C, and the flat nature in the Prato \*\* is also a quite good result, and this component system found that it was promising practically.

[0017] The pressure (Prato equilibrium pressure) of the flat field of the pressure composition constant-temperature line changes with the composition ratios of Ti/Cr, as shown in drawing 8 (a) and (b). This drawing fixes Mo of an Ti-Cr-Mo system to 7at(s)%, and changes the amount of Ti and Cr. They are 0.01MPa(s) at the alloy composition which shows the absorption pressure of 10 or less MPas by this invention at -40 degrees C considered as an operating environment of applications, such as a hydrogen tank and heat pump, and 100 degrees C. Alloy composition which shows the above desorption pressure was made into the generic claim.

[0018] Moreover, the hydrogen absorption and discharge process (PCT property) of a sample which heat treatment of water quenching was performed to drawing 4 after 2-hour maintenance at 1400 degrees C after the arc dissolution like the above about Ti<sub>41</sub>Cr<sub>56</sub> W<sub>3</sub> are shown. This drawing shows 40-degree C maximum hydrogen storage capacity about 2.3 Wt(s)%, it shows an about 2.4 Wt(s)% good value at 0 degree C, and 40 degrees C shows the result also with the quite good flat nature in the Prato \*\* also in the emission characteristic. drawing 3 and drawing 4 -- abbreviation -- it is the same hydrogen-absorption property, and from this, by W, since it is twice [ about ] the atomic weight of this as compared with Mo, an addition is considered that a BCC-ized effect is because it is fully obtained at least Comparison of hydrogen \*\*\*\*\* of this invention material and comparison material is shown in Table 1.

[0019]

[Table 1]

試料	組成	水素吸蔵量(cc/g)	水素放出量(cc/g)
発明材	Ti <sub>33</sub> Cr <sub>60</sub> Mo <sub>7</sub>	598	423
	Ti <sub>36</sub> Cr <sub>57</sub> Mo <sub>7</sub>	674	502
比較材	Ti <sub>20</sub> Cr <sub>73</sub> Mo <sub>7</sub>	146	40

[0020] From this table, it is Ti33Cr60Mo7 of this invention. A burst size is 598 cc/g in 598 cc/g then, and hydrogen storage capacity is Ti36Cr57Mo7. Hydrogen storage capacity is 674 cc/g then, and the burst size shows 502 cc/g and the good value. On the other hand, at Ti20Cr73Mo7 of comparison material, as for the burst size, hydrogen storage capacity shows the quite small value by 146 cc/g as compared with 40 cc/g and the aforementioned this invention material. Clearly, this invention material has more available-hydrogen movement magnitude than a RABESU alloy, is excellent in hydrogen \*\*\*\*\*, and is the BCC alloy and this level containing V of the former [ weighted solidity / the ]. moreover, the table 2 -- composition \*\*Ti36Cr57Mo7 \*\*\*\*\* -- comparison shows the phase molar fraction of the BCC and the Laves phase by XRD after a hardener and heat treatment

[0021] The chart of the X-ray relative intensity of XRD (Cu electrode, output 48kv) about Ti41Cr56 W3 and the degree of angle of diffraction is shown in drawing 7 (a) and (b). (a) Drawing is a sample immediately after the arc dissolution, and the (b) view is a result about heat treatment material (1400 degrees C -> water cooling). Although the phase existed in addition to this with the Laves phase immediately after the arc dissolution, it turns out that it is BCC uniform single phase with heat treatment.

[0022]

[Table 2]

	BCC	ラーベス
母合金	0	100
1300℃×2hr-油冷	86	14

[0023] The alloy heat-treated from this to a hardener being RABESU single phase is understood that it has BCC-ized notably.

[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing in which showing composition by drawing shown on the 3 yuan state diagram of the TiCrX (Mo and/or W) system of this invention, and showing example composition of (a) composition range and (b) TiCrMo system.

[Drawing 2] It is the PCT view showing hydrogen \*\*\*\*\* by composition of the TiCrMo system concerning the example of this invention.

[Drawing 3] It is the PCT view showing hydrogen \*\*\*\*\* in 0 degree C of the TiCrMo system concerning the example of this invention, and 40 degrees C.

[Drawing 4] It is the PCT view showing hydrogen \*\*\*\*\* in 0 degree C of the TiCrW system concerning the example of this invention, and 40 degrees C.

[Drawing 5] It is a TiCr<sub>2</sub>-X pseudo-binary diagram about the heat treatment range of this invention.

[Drawing 6] It is a Ti-Cr system binary-condition view relevant to this invention.

[Drawing 7] It is the chart of XRD of the TiCrW system concerning the example of this invention, and is a thing immediately after (a) arc dissolution and after (b) heat treatment.

[Drawing 8] It is drawing in which showing the relation of the Prato equilibrium pressure and the amount of Cr(s) concerning the example of this invention, and showing a (a)-40 degree C absorption pressure and (b)100 degree C desorption pressure.

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[Translation done.]



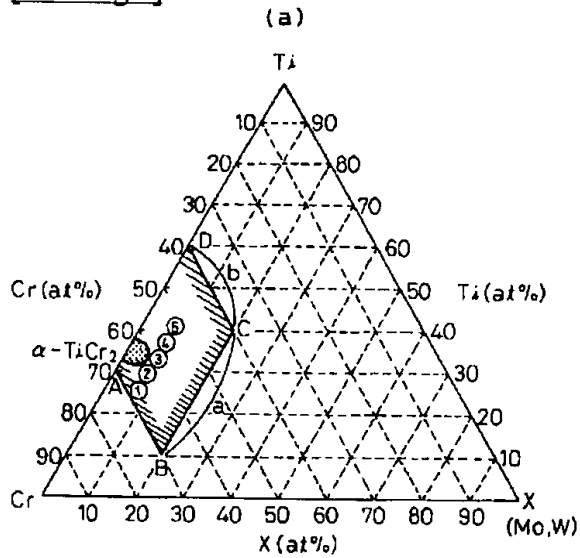
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DRAWINGS

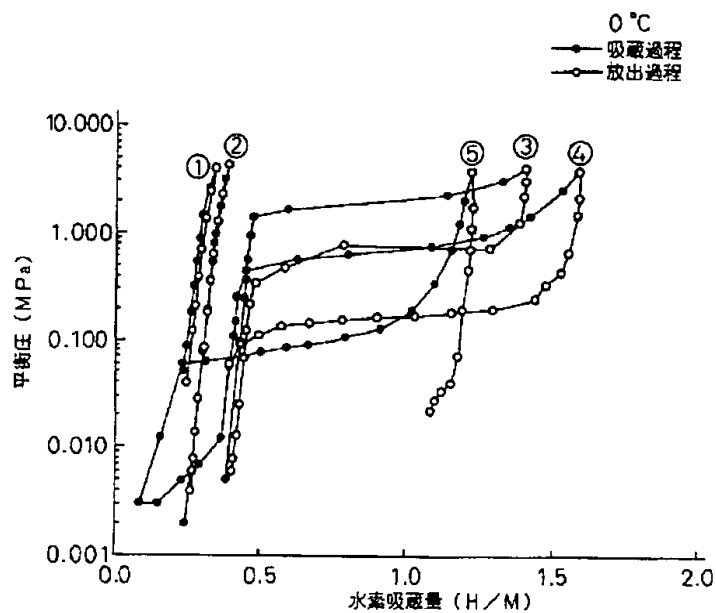
[Drawing 1]



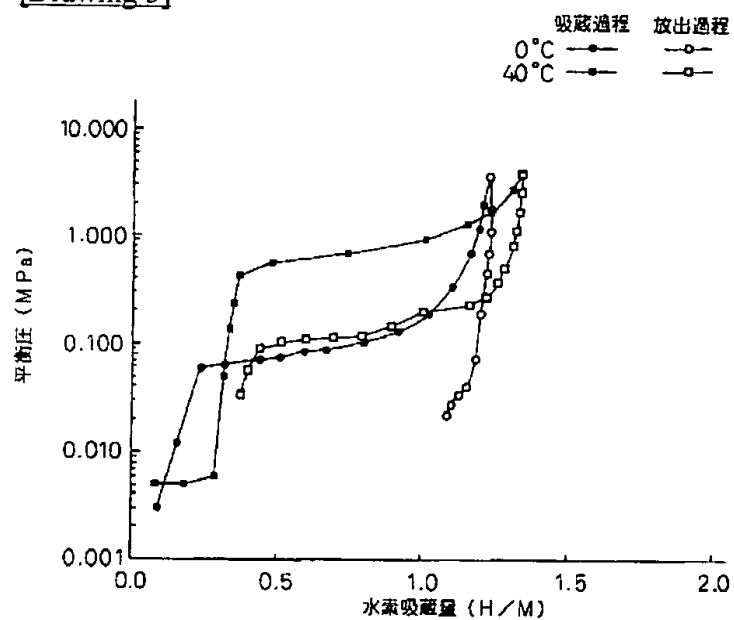
(b)

	(at%)		
	Ti	Cr	X
①	27	66	7
②	30	63	7
③	33	60	7
④	36	57	7
⑤	39	54	7

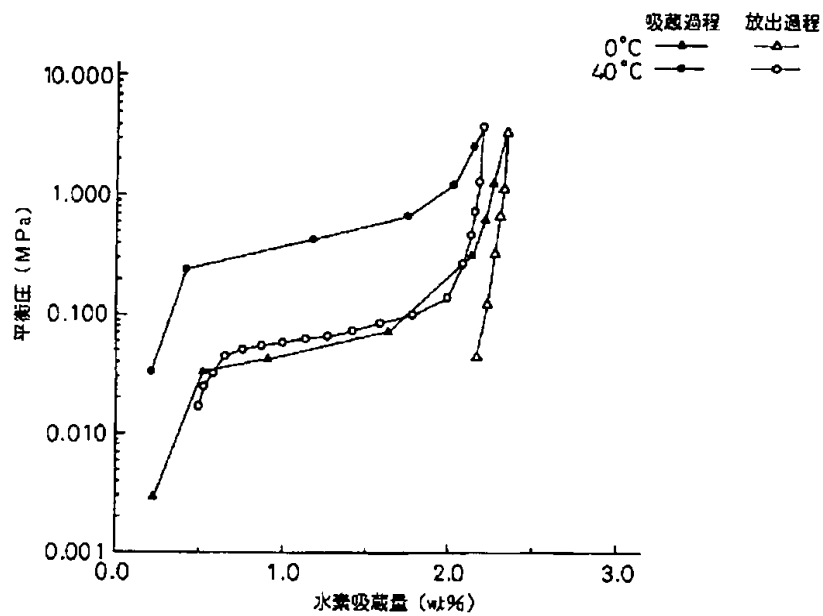
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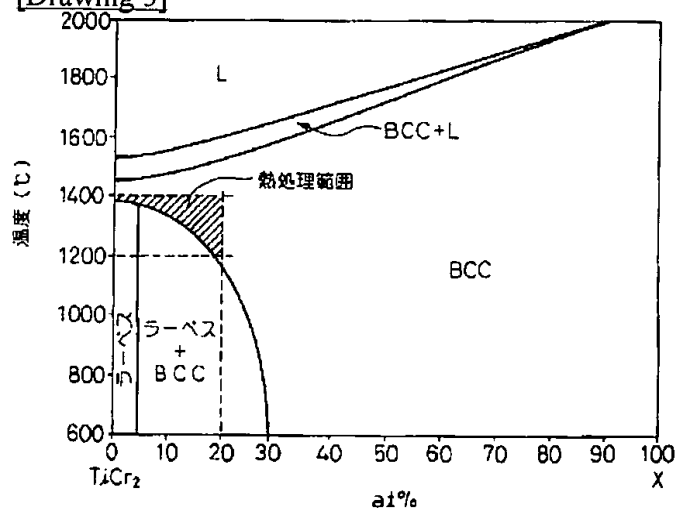
[Drawing 3]



[Drawing 4]

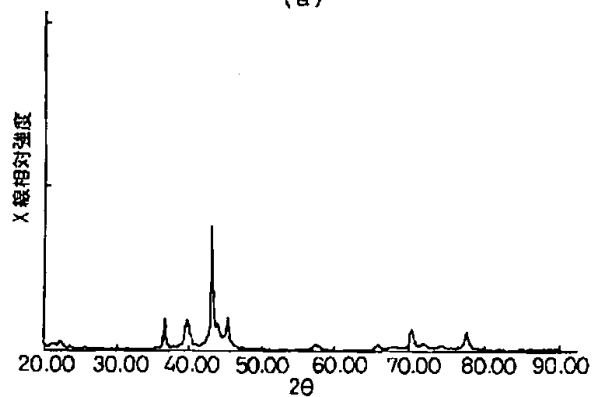


[Drawing 5]

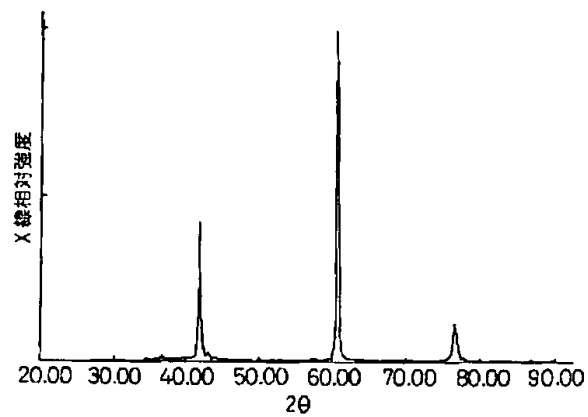


[Drawing 7]

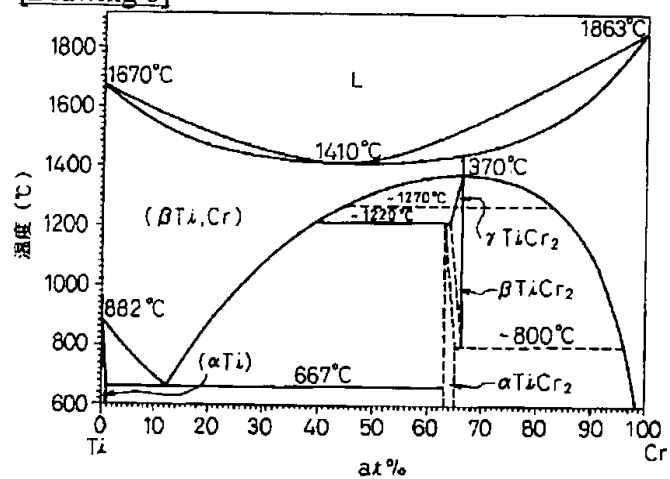
(a)



(b)

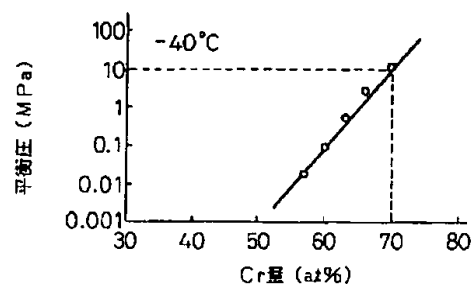


[Drawing 6]

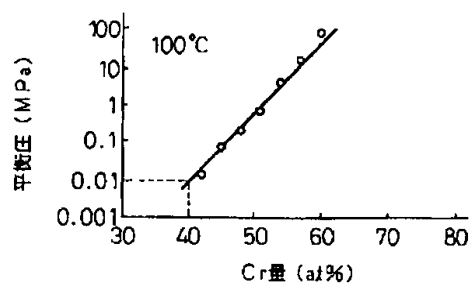


[Drawing 8]

(a)



(b)



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[Translation done.]